

METHOD OF MAKING NANO-PARTICLES OF SELECTED SIZE DISTRIBUTION

BACKGROUND OF THE INVENTION

The present invention relates to polymer nanoparticles, methods for their preparation, and their use as, for example, additives for rubber, and particularly, tire compositions. The invention advantageously provides mechanisms for surface modifications, functionalization, and general characteristic tailoring to improve
5 performance in various polymer compositions.

Polymer nanoparticles have attracted increased attention over the past several years in a variety of fields including catalysis, combinatorial chemistry, protein supports, magnets, and photonic crystals. Similarly, vinyl aromatic (e.g. polystyrene) microparticles have been prepared for use as a reference standard in the calibration of
10 various instruments, in medical research and in medical diagnostic tests. Such polystyrene nanoparticles have been prepared by anionic dispersion polymerization and emulsion polymerization. However, controlling the size of nanoparticles during polymerization and/or the surface characteristics of such nanoparticles can be difficult.

Rubbers may be advantageously modified by the addition of various polymer
15 compositions. The physical properties of rubber moldability and tenacity are often improved through such modifications. Of course, however, the simple indiscriminate addition of nanoparticles to rubber is likely to cause degradation of the matrix material, i.e., the rubber. Nonetheless, it is expected that the selection of nanoparticles having

suitable size, material composition, and surface chemistry, etc., will improve the matrix characteristics.

In this regard, development of nanoparticles having a outer layer which would be compatible with a wide variety of matrix materials is desirable because discrete particles could likely disperse evenly throughout the host to provide a uniform matrix composition. However, the development of a process capable of reliably producing acceptable nanoparticles has been a challenging endeavor. For example, the solubility of various monomers in traditional alkane solvents has made solution polymerization a difficult process by which to achieve nanoparticles having a desirable outer layer.

Moreover, the development of a solution polymerization process producing reliable nanoparticles, particularly nanoparticles advantageously employed in rubber compositions, has been elusive.

Commonly owned U.S. Patent Number 6,437,050 is directed to polymer nanoparticles and a method of forming nanoparticles with desired surface characteristics and size. Commonly owned U.S. Patent Application Serial Number 10/223,393 (filed August 19, 2002) includes a method of controlling the surface characteristics of polymer nanoparticles via surface functionalization. Each of these is directed to the formation of nanoparticles having uniform sizes and each is herein incorporated by reference. In addition to the nanoparticles disclosed therein, it would be desirable to develop a process for forming polymer nanoparticles with a broad and controllable size distribution. It would also be desirable to develop a batch process for forming polymer nanoparticles with bimodal or trimodal size distributions.

SUMMARY OF THE INVENTION

A process for forming a nanoparticle composition is provided. The process includes polymerizing conjugated diene monomer in a hydrocarbon solvent to form a first reaction mixture, and charging one or both of additional alkenylbenzene monomer
5 in excess of the conjugated diene monomer and anionic catalyst to form mono-block and diblock polymers. Micelles of the mono-block and diblock polymers are formed, and at least one crosslinking agent is added to cross-link the micelles and form nanoparticles. The nanoparticles preferably have a poly(alkenylbenzene) core and an outer layer including monomer units selected from the group consisting of conjugated
10 dienes, alkylenes, and mixtures thereof, and a size distribution of between about 1 and 1000 nm. Preferably, the process will be performed in a single batch type procedure.

A polymer nanoparticle composition having nanoparticles with a size distribution between about 1 nm and 1000 nm, and a polydispersity index between about 1 and 10 is provided. Preferably, the polydispersity index will be between about 1.5 and 8.0. The
15 nanoparticles preferably include an outer layer having monomer units selected from the group consisting of alkenylbenzenes, conjugated dienes, alkylenes, and mixtures thereof, and an inner layer including alkenyl monomer units. The nanoparticles include mono-block and diblock polymer chains.

A rubber composition is provided. The composition includes rubber and polymer
20 nanoparticles having a size distribution between about 1 and 1000 nm. The polymer nanoparticles preferably have an outer layer including monomer units selected from the group consisting of conjugated dienes, alkenylbenzenes, alkylenes, and mixtures thereof, and an inner layer including alkenylbenzene monomer units.

BRIEF DESCRIPTION OF THE DRAWINGS

FIGURE 1 is a GPC analysis result of polymer nanoparticles formed in accordance with EXAMPLE 4.

5 FIGURE 2 is a transmission electron microscopy (TEM) photograph of polymer nanoparticles formed in accordance with EXAMPLE 4.

DETAILED DESCRIPTION OF ILLUSTRATIVE EMBODIMENTS

GENERAL NANOPARTICLE PROCESS OF FORMATION

10 Nanoparticles affect properties of the host composition. For example, larger nanoparticles impart good wear characteristics to host compositions, while smaller nanoparticles impart good reinforcement characteristics. It is often desirable to include nanoparticles of different sizes in host compositions. Previously, nanoparticles of different sizes had to be formed individually, resulting in longer preparation times and
15 the higher costs associated with performing multiple reactions.

Exemplary polymer nanoparticle compositions of the present invention include nanoparticles having a size distribution between about 1 nm and 1000 nm. In one embodiment the size distribution is random. In another embodiment the size distribution is bimodal. It may also be desirable to have a distribution that is trimodal, quadramodal,
20 etc. The individual nanoparticles are formed from diblock polymer chains having at least a poly(conjugated diene) block and a poly(alkenylbenzene) block and monoblock polymer chains having a poly(alkenylbenzene) block. The poly(alkenylbenzene) blocks may be crosslinked to form the desired nanoparticles. The polymer nanoparticles of the

present invention preferably have a dispersity between about greater than 1 and 10, wherein the dispersity is represented by the ratio of M_w to M_n , with a ratio of 1 being substantially monodisperse. Preferably, polydispersity will fall between about 1.15 and 8.0, more preferably between about 1.5 and 6. Moreover, the nanoparticles are
5 preferably spherical, though slight shape defects are acceptable, provided the nanoparticles generally retain their discrete nature with little or no polymerization between particles.

The nanoparticles are preferably formed via dispersion polymerization, although emulsion polymerization is also contemplated. Hydrocarbons are preferably used as
10 the dispersion solvent. Suitable solvents include aliphatic hydrocarbons, such as pentane, hexane, heptane, octane, nonane, decane, and the like, as well as alicyclic hydrocarbons, such as cyclohexane, methyl cyclopentane, cyclooctane, cyclopentane, cycloheptane, cyclononane, cyclodecane and the like. These hydrocarbons may be used individually or in combination. However, as more fully described herein below,
15 selection of a solvent in which one polymer forming the nanoparticles is more soluble than another polymer forming the nanoparticles is important in micelle formation.

With respect to the monomers and solvents identified herein, nanoparticles are formed by maintaining a temperature that is favorable to polymerization of the selected monomers in the selected solvent(s). Preferred temperatures are in the range of about
20 -40 to 250 °C, with a temperature in the range of about 0 to 150 °C being particularly preferred. As described in more detail below, the interaction of monomer selection, temperature, and solvent facilitates the formation of block polymers which form micelles and ultimately the desired nanoparticles.

One method for forming the present polymer nanoparticles includes forming a first polymer of conjugated diene monomers in the hydrocarbon solvent. After formation of the first polymer, a second monomer is added to the polymerization, along with additional initiator. The second monomer polymerizes onto the first polymer to form a diblock polymer as well as forming a separate second polymer which is a mono-block polymer. The diblock polymer contains at least a first end block that is soluble in the dispersion solvent, preferably a conjugated diene monomer, and a second end block which is less soluble in the dispersion solvent, preferably a vinyl-substituted aromatic hydrocarbon monomer. In a preferred embodiment, a vinyl-substituted aromatic hydrocarbon is chosen which as a polymer is generally insoluble in the dispersion solvent.

The multi-block polymer preferably has M_w of about 5,000 to 10,000,000 more preferably between about 10,000 and 200,000. A typical multi-block polymer will be comprised of 5 to 95% by weight conjugated diene and 5 to 95% by weight vinyl-substituted aromatic hydrocarbon, more preferably 20 to 80% by weight, and most preferably 30 to 70% by weight of each contributed monomer type. Each multi-block preferably has M_w between about 1,000 and 10,000,000, more preferably between about 2,000 and 5,000,000. The monoblock polymer preferably has a M_w between about 2,000 and 200,000, more preferably between about 5,000 and 100,000.

The size distribution of the nanoparticles may be controlled by manipulating the ratio of diblock to mono-block polymer chains as well as the molecular weights of the blocks. This ratio may be manipulated by altering the amount of initiator and/or monomer added during each step of the polymerization process. For example, a

greater amount of initiator added during the polymerization of the conjugated diene monomer than added during the polymerization of the alkenylbenzene monomer would favor diblock formation over mono-block formation, resulting in a greater number of large nanoparticles. Similarly, a greater amount of alkenylbenzene monomer added relative to the conjugated diene, will result in the formation of a wider particle size distribution. In this regard, the ratio of conjugated diene to alkenylbenzene will preferably be less than 1:1. More preferably, the ratio will be between about 0.1:1 and 0.8:1. More preferably, the ratio will be between about 0.2:1 and 0.7:1. Conversely, a greater amount of initiator added during the polymerization of the alkenylbenzene monomer than added during the polymerization of the conjugated diene monomer would favor mono-block formation over diblock formation, resulting in a greater number of small nanoparticles. The weight ratio of mono-blocks to diblocks can be from 99 to 1:1 to 99, preferably to 90 to 10:10 to 90, more preferably 80 to 20:20 to 80.

Without being bound by theory, it is believed that at least a bimodal nano-particle size distribution results because the micelle formation of mono- and diblocks is a bimodal distribution.

According to one embodiment of the invention, diblock polymers are formed of vinyl aromatic hydrocarbon monomers and conjugated diene monomers in the hydrocarbon solvent. The diblock polymers contain at least a first end block that is soluble in the dispersion solvent, preferably a conjugated diene monomer, and at least a second end block which is less soluble in the dispersion solvent, preferably a vinyl-substituted aromatic hydrocarbon monomer. Moreover, in one preferred embodiment, a vinyl-substituted aromatic hydrocarbon monomer is chosen, the polymer of which is

generally insoluble in the dispersion solvent. It is also noted that the formation of polydisperse nanoparticles can be enhanced by the use of a relatively high monomer concentration during polymerization. Moreover, it is desirable to maintain a monomer concentration level of at least about 10%, preferably at least about 20%.

5 As is known in the art, such polymers may be formed by living anionic polymerization, in which a vinyl-substituted aromatic hydrocarbon monomer is added to a completely polymerized conjugated diene monomer. Another method of forming substantially diblock polymers is the living anionic copolymerization of a mixture of monomers, such as a conjugated diene monomer and a vinyl-substituted aromatic
10 hydrocarbon monomer in a hydrocarbon solvent, particularly, in the absence of certain polar additives, such as ethers, tertiary amines, or metal alkoxides which could otherwise effect the polymerization of the separately constituted polymer blocks. Under these conditions, the conjugated diene generally polymerizes first, followed by the polymerization of the vinyl-substituted aromatic hydrocarbon. Of course, certain
15 advantages, as described below may be achieved via a random polymerization of at least one block of the polymer.

Nonetheless, it is generally preferred that a vinyl substituted aromatic hydrocarbon polymerize last, positioning the living end of the polymerizing polymer on a vinyl aromatic block to facilitate later cross-linking.

20 Such polymers, formed by either method, are believed to aggregate to form micelle-like structures with, for example, vinyl-substituted aromatic blocks directed toward the centers of the micelles and conjugated diene blocks as tails extending therefrom. It is noted that a further hydrocarbon solvent charge or a decrease in

polymerization mixture temperature may also be used, and may in fact be required, to obtain formation of the micelles. Moreover, these steps may be used to take advantage of the general insolubility of the vinyl-aromatic blocks. An exemplary temperature range for micelle formation is between about 40 and 100 °C, more preferably between about 50 and 80 °C.

After the micelles have formed, additional conjugated diene monomer and/or vinyl-substituted aromatic hydrocarbon monomer can be added to the polymerization mixture as desired.

After formation of the micelles, a cross-linking agent is added to the polymerization mixture. Preferably, a crosslinking agent is selected which has an affinity to the vinyl-substituted aromatic hydrocarbon monomer blocks and migrates to the center of the micelles due to its compatibility with the monomer units and initiator residues present in the center of the micelle and its relative incompatibility with the dispersion solvent and monomer units present in the outer layer of the micelle. The crosslinking agent crosslinks the center core of the micelle (i.e. alkenylbenzene) to form the desired nanoparticle. Consequently, nanoparticles are formed from the micelles with a core including, for example, styrene monomer units and a outer layer including, for example, butadiene monomer units.

The conjugated diene monomers contemplated for the block polymer are those soluble in non-aromatic hydrocarbon solvents. C₄-C₈ conjugated diene monomers are the most preferred. Exemplary conjugated diene monomers include 1,3-butadiene, isoprene, 1,3-pentadiene, 2,3-dimethyl-1,3-butadiene, 1,3-hexodiene, 2-methyl-1,3-pentadiene, 3,4-dimethyl-1,3-hexodiene, 4,5-diethyl-1,3-octadiene, phenyl-1,3-

butadiene, and mixtures thereof. An especially preferred conjugated diene is 1,3-butadiene.

Vinyl-substituted aromatic hydrocarbon monomers include styrene, α -methylstyrene, 1-vinyl naphthalene, 2-vinyl naphthalene, 1- α -methyl vinyl naphthalene, 2- α -methyl vinyl naphthalene, vinyl toluene, methoxystyrene, t-butoxystyrene, and the like, as well as alkyl, cycloalkyl, aryl, alkaryl, and aralkyl derivatives thereof, in which the total number of carbon atoms in the combined hydrocarbon is not greater than 18, as well as any di- or tri-vinyl substituted aromatic hydrocarbons, and mixtures thereof.

The micelle formed by the polymerization of vinyl-substituted aromatic hydrocarbons and conjugated diene monomers is preferably crosslinked to enhance the uniformity and permanence of shape and size of the resultant nanoparticle. Preferred crosslinking agents are di- or tri-vinyl-substituted aromatic hydrocarbons. However, crosslinking agents which are at least bifunctional, wherein the two functional groups are capable of reacting with vinyl-substituted aromatic hydrocarbon monomers are acceptable. A preferred crosslinking agent is divinylbenzene (DVB).

A 1,2-microstructure controlling agent or randomizing modifier is optionally used to control the 1,2-microstructure in the conjugated diene contributed monomer units, such as 1,3-butadiene, of the nanoparticle. Suitable modifiers include hexamethylphosphoric acid triamide, N,N,N',N'-tetramethylethylene diamine, ethylene glycol dimethyl ether, diethylene glycol dimethyl ether, triethylene glycol dimethyl ether, tetraethylene glycol dimethyl ether, tetrahydrofuran, 1,4-diazabicyclo [2.2.2] octane, diethyl ether, triethylamine, tri-n-butylamine, tri-n-butylphosphine, p-dioxane, 1,2-dimethoxy ethane, dimethyl ether, methyl ethyl ether, ethyl propyl ether, di-n-propyl

ether, di-n-octyl ether, anisole, dibenzyl ether, diphenyl ether, dimethylethylamine, bis-oxalanyl propane, tri-n-propyl amine, trimethyl amine, triethyl amine, N,N-dimethyl aniline, N-ethylpiperidine, N-methyl-N-ethyl aniline, N-methylmorpholine, tetramethylenediamine, oligomeric oxolanyl propanes (OOPs), 2,2-bis-(4-methyl dioxane), and bistetrahydrofuryl propane. A mixture of one or more randomizing modifiers also can be used. The ratio of the modifier to the monomers can vary from a minimum as low as 0 to a maximum as great as about 4000 millimoles, preferably about 0.01 to 3000 millimoles, of modifier per hundred grams of monomer currently being charged into the reactor. As the modifier charge increases, the percentage of 1,2- microstructure (vinyl content) increases in the conjugated diene contributed monomer units in the outer layer of the polymer nanoparticle. The 1,2-microstructure content of the conjugated diene units is preferably between about 5 and 95%, more preferably between about 1 and 99%.

Without being bound by theory, it is believed that an exemplary micelle will be comprised of ten to five hundred block polymers yielding, after crosslinking, a nanoparticle having a M_w of between about 5,000 and 10,000,000, preferably between about 5,000 and 4,500,000.

STRUCTURAL MODIFICATIONS

In an alternative embodiment, an outer layer of the polymer nanoparticle is a copolymer including at least one alkenylbenzene monomer unit and at least one conjugated diene monomer unit. The copolymer may be random or ordered. Accordingly, the outer layer may include an SBR rubber or SI rubber. Herein

throughout, references to a poly (conjugated diene) outer layer are understood to include copolymers of the type described here.

HYDROGENATION OF A NANOPARTICLE OUTER LAYER

5 After micelle formation, or alternatively, after crosslinking, the polydiene blocks may be hydrogenated to form a modified outer layer. A hydrogenation step may also be carried out after functionalization of the nanoparticles. A hydrogenation step may be carried out by methods known in the art for hydrogenating polymers, particularly polydienes. A preferred hydrogenation method includes placing the crosslinked
10 nanoparticles in a hydrogenation reactor in the presence of a catalyst. After the catalyst has been added to the reactor, hydrogen gas (H_2) is charged to the reactor to begin the hydrogenation reaction. The pressure is adjusted to a desired range, preferably between about 10 and 3000 kPa, more preferably between about 50 and 2600 kPa. H_2 may be charged continuously or in individual charges until the desired conversion is
15 achieved. Preferably, the hydrogenation reaction will reach at least about 20% conversion, more preferably greater than about 85% conversion. The conversion reaction may be monitored by 1H NMR.

Preferred catalysts include known hydrogenation catalysts such as Pt, Pd, Rh, Ru, Ni, and mixtures thereof. The catalysts may be finely dispersed solids or absorbed
20 on inert supports such as carbon, silica, or alumina. Especially preferred catalysts are prepared from nickel octanoate, nickel ethylhexanoate, and mixtures thereof.

The outer layer formed by an optional hydrogenation step will vary depending on the identity of the monomer units utilized in the formation of the nanoparticle outer layer,

particularly the poly (conjugated diene) blocks. For example, if the poly(conjugated diene) block contains 1,3-butadiene monomer units, the resultant nanoparticle layer after hydrogenation will be a crystalline poly(ethylene) layer. In another embodiment, a layer may include both ethylene and propylene units after hydrogenation if the non-
5 hydrogenated poly (conjugated diene) block contains isoprene monomer units. It should be noted that the non-hydrogenated poly (conjugated diene) block may contain a mixture of conjugated diene monomer units, or even alkenylbenzene units, resulting in a mixture of monomer units after hydrogenation.

10 INITIATORS

The present inventive process is preferably initiated via addition of anionic initiators that are known in the art as useful in the copolymerization of diene monomers and vinyl aromatic hydrocarbons. Exemplary organo-lithium catalysts include lithium compounds having the formula $R(Li)_x$, wherein R represents a C_1 - C_{20} hydrocarbyl
15 radical, preferably a C_2 - C_8 hydrocarbyl radical, and x is an integer from 1 to 4. Typical R groups include aliphatic radicals and cycloaliphatic radicals. Specific examples of R groups include primary, secondary, and tertiary groups, such as n-propyl, isopropyl, n-butyl, isobutyl, t-butyl, etc.

Specific examples of exemplary initiators include ethyllithium, propyllithium, n-
20 butyllithium, sec-butyllithium, tert-butyllithium, and the like; aryllithiums, such as phenyllithium, tolyllithium, and the like; alkenyllithiums such as vinylithium, propenyllithium, and the like; alkylene lithium such as tetramethylene lithium, pentamethylene lithium, and the like. Among these, n-butyllithium, sec-butyllithium, tert-

butyllithium, tetramethylene lithium, and mixtures thereof are preferred. Other suitable lithium initiators include one or more of: *p*-tolyllithium, 4-phenylbutyl lithium, 4-butylcyclohexyl lithium, 4-cyclohexylbutyl lithium, lithium dialkyl amines, lithium dialkyl phosphines, lithium alkyl aryl phosphine, and lithium diaryl phosphines.

5 Functionalized lithium inhibitors are also contemplated as useful in the present invention. Preferred functional groups include amines, formyl, carboxylic acids, alcohol, tin, silicon, silylether, tin-functionalized, and mixtures thereof. A nanoparticle including diblock polymers initiated with a functionalized initiator may include functional groups on the surface of the nanoparticle. For example, when block polymers are initiated by
10 hexamethylene imine propyllithium, the initiator residue remaining at the beginning of the polymer chain will contain an amine group. Once the polymer chains have aggregated and have been crosslinked, the resultant nanoparticles will contain amine groups on or near the nanoparticle surface.

 It may be desirable to utilize functionalized initiators during only one of the initiator
15 charges of the present invention, thereby resulting in functionalization of only one size nanoparticle. Alternatively, differently functionalized initiators may be utilized during each charge, resulting in different functionalization on each size nanoparticle.

 Anionic initiators generally are useful in amounts ranging from about 0.01 to 60 millimoles per hundred grams of monomer charge.

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POLYMER NANOPARTICLE APPLICATIONS

 A variety of applications are contemplated for use in conjunction with the nanoparticles of the present invention. Furthermore, the several mechanisms described

herein for modifying the nanoparticles render them suitable for different applications. All forms of the present inventive nanoparticles are, of course, contemplated for use in each of the exemplary applications and all other applications envisioned by the skilled artisan.

5

GENERAL RUBBER

After the polymer nanoparticle composition has been formed, it may be blended with a rubber to improve the physical characteristics of the rubber composition.

Nanoparticles are useful modifying agents for rubbers because they are discrete particles which are capable of dispersing uniformly throughout the rubber composition, resulting in uniformity of physical characteristics. Furthermore, certain of the present nanoparticles are advantageous because the outer layer of poly(conjugated diene), especially vinyl-modified poly(conjugated diene), is capable of bonding with the rubber matrix due to the accessibility of the double bonds in the poly(conjugated diene).

The present polymer nanoparticles are suitable for modifying a variety of rubbers including, but not limited to, random styrene/butadiene copolymers, butadiene rubber, poly(isoprene), nitrile rubber, polyurethane, butyl rubber, EPDM, and the like.

Advantageously, the inclusion of the present nanoparticles have demonstrated rubbers having improved tensile and tear strength of at least about 30% over a rubber modified with non-spherical copolymers.

Furthermore, nanoparticles with hydrogenated outer layers may demonstrate improved compatibility with specific rubbers. For example, nanoparticles including a hydrogenated polyisoprene outer layer may demonstrate superior bonding with and

improved dispersion in an EPDM rubber matrix due to the compatibility of hydrogenated isoprene with EPDM rubber.

Additionally, nanoparticles with copolymer surfaces may demonstrate improved compatibility with rubbers. The copolymer tails with the outer layer of the nanoparticles
5 may form a brush-like surface. The host composition is then able to diffuse between the tails allowing improved interaction between the host and the nanoparticles.

TIRE RUBBER

One application for nanoparticle containing rubber compounds is in tire rubber
10 formulations.

Vulcanizable elastomeric compositions of the invention may be prepared by mixing a rubber, a functionalized nanoparticle composition, with a reinforcing filler comprising silica, or a carbon black, or a mixture of the two, a processing aid and/or a coupling agent, a cure agent, and an effective amount of sulfur to achieve a satisfactory
15 cure of the composition.

Preferred rubbers are conjugated diene polymers, copolymers, or terpolymers of conjugated diene monomers and monovinyl aromatic monomers, can be utilized as 100 parts of the rubber in the tread stock compound, or they can be blended with any conventionally employed treadstock rubber which includes natural rubber, synthetic
20 rubber and blends thereof. Such rubbers are well known to those skilled in the art and include synthetic polyisoprene rubber, styrene-butadiene rubber (SBR), styrene-isoprene rubber, styrene-isoprene-butadiene rubber, butadiene-isoprene rubber, polybutadiene, butyl rubber, neoprene, acrylonitrile-butadiene rubber (NBR), silicone

rubber, the fluoroelastomers, ethylene acrylic rubber, ethylene-propylene rubber, ethylene-propylene terpolymer (EPDM), ethylene vinyl acetate copolymer, epichlorohydrin rubber, chlorinated polyethylene-propylene rubbers, chlorosulfonated polyethylene rubber, hydrogenated nitrile rubber, tetrafluoroethylene-propylene rubber and mixtures thereof.

Examples of reinforcing silica fillers which can be used in the vulcanizable elastomeric composition include wet silica (hydrated silicic acid), dry silica (anhydrous silicic acid), calcium silicate, and the like. Other suitable fillers include aluminum silicate, magnesium silicate, and the like. Among these, precipitated amorphous wet-process, hydrated silicas are preferred. Silica can be employed in the amount of about one to about 100 parts per hundred parts of the elastomer, preferably in an amount of about 5 to 80 phr and , more preferably, in an amount of about 30 to about 80 phrs. The useful upper range is limited by the high viscosity imparted by fillers of this type. Some of the commercially available silica which can be used include, but are not limited to, HiSil[®] 190, HiSil[®] 210, HiSil[®] 215, HiSil[®] 233, HiSil[®] 243, and the like, produced by PPG Industries (Pittsburgh, PA). A number of useful commercial grades of different silicas are also available from DeGussa Corporation (e.g., VN2, VN3), Rhone Poulenc (e.g., Zeosil[®] 1165MP), and J.M. Huber Corporation.

Including surface functionalized nanoparticles in silica containing rubber compositions has been shown to decrease the shrinkage rates of such silica containing rubber compositions. Maleated nanoparticles may be compounded in silica compositions in concentrations up to about 30 wt% of the total composition, more preferably up to about 40 wt%, most preferably up to about 50 wt%.

The rubber can be compounded with all forms of carbon black, optionally additionally with silica. The carbon black can be present in amounts ranging from about one to about 100 phr. The carbon blacks can include any of the commonly available, commercially-produced carbon blacks, but those have a surface area of at least 20 m²/g and, or preferable, at least 35m²/g up to 200m²/g or higher are preferred. Among useful carbon blacks are furnace black, channel blacks, and lamp blacks. A mixture of two or more of the above blacks can be used in preparing the carbon black products of the invention. Typical suitable carbon black are N-110, N-220, N-339, N-330, N-352, N-550, N-660, as designated by ASTM D-1765-82a.

Certain additional fillers can be utilized including mineral fillers, such as clay, talc, aluminum hydrate, aluminum hydroxide and mica. The foregoing additional fillers are optional and can be utilized in the amount of about 0.5 phr to about 40 phr.

Numerous coupling agents and compatibilizing agents are known for use in combining silica and rubber. Among the silica-based coupling and compatibilizing agents include silane coupling agents containing polysulfide components, or structures such as, for example, trialkoxyorganosilane polysulfides, containing from about 2 to about 8 sulfur atoms in a polysulfide bridge such as, for example, bis-(3-triethoxysilylpropyl) tetrasulfide (Si69), bis-(3-triethoxysilylpropyl) disulfide (Si75), and those alkyl alkoxysilanes of the such as octyltriethoxy silane, hexyltrimethoxy silane.

It is readily understood by those having skill in the art that the rubber composition would be compounded by methods generally known in the rubber compounding art, such as mixing the various vulcanizable polymer(s) with various commonly used additive materials such as, for example, curing agents, activators, retarders and

accelerators, processing additives, such as oils, resins, including tackifying resins, plasticizers, pigments, additional fillers, fatty acid, zinc oxide, waxes, antioxidants, anti-ozonants, and peptizing agents. As known to those skilled in the art, depending on the intended use of the sulfur vulcanizable and sulfur vulcanized material (rubbers), the additives mentioned above are selected and commonly used in the conventional amounts.

Specifically, the above-described nanoparticle containing rubber compounds are contemplated for use in rubber compounds used to make tire treads and side walls due to the enhanced reinforcement capabilities of the present nanoparticles. The higher dynamic modulus (G') and its lower temperature dependence along with the lower hysteresis values at high temperature leads to the improved cornering, handling, dry, snow, and wet traction, rolling resistance, dispersion, and aging properties of the resultant tire compositions. Improved aging properties, thermal aging (high temperature) or mechanical aging (static or dynamic deformation cycles), include retention of the G' modulus, hysteresis, mechanical strengths, etc. Tin-functionalized nanoparticles are especially suited for use in tire compositions. Nanoparticles including a copolymer outer layer are also suitable for use in such tire compositions, because the longer copolymer chains in the outer layer leads to greater diffusion of the host rubber composition into the outer layer of the nanoparticle.

EXAMPLES

The following examples are provided to better illustrate the invention. The Examples are not intended to limit the envisioned scope of the invention as defined by the appended claims.

5 A 7.5 L reactor equipped with external jacket heating and internal agitation was used for all polymerization. Butadiene in hexane (blend-35, 21.8 wt% butadiene), styrene in hexane (33 wt% styrene), hexane, butyllithium (1.68 M) and BHT were used as supplied from Firestone Synthetic Company. Technical grade divinylbenzene (80 %, mixture of isomers, Aldrich) was stored on aluminum oxide beads and calcium hydride
10 under N₂.

Example 1.

The reactor was charged with 0.50 kg hexane and 1.04 kg butadiene blend B-35. The jacket was heated to 57 °C. When the batch reached 57 °C, 5.0 mL of 1.68 M
15 butyllithium diluted with about 20 mL of hexane were added. The polymerization exothermed after 15 minutes of reaction. After 2 hours, 0.68 kg styrene blend were added to the reactor, while maintaining the jacket temperature at 57 °C. An exothermic peak was observed after 15 minutes. After 2 hrs, 1.8 kg hexane was added, in order to favor the formation of micelles. After about 15 min, 50 mL of divinylbenzene was added
20 to the reaction mixture. After 2 hours, the reaction mixture was cooled down and dropped in an isopropanol/acetone solution (about 500 mL/2L) containing BHT. The solid was then filtered through cheesecloth and drum-dried.

GPC analysis of the products, based on a polystyrene/THF standard, indicated a mean average molecular weight (M_n) of 962,000. The polydispersity index was 1.08, which suggests that the particles were monodisperse.

5 Example 2.

The reactor was charged with 0.50 kg hexane and 1.04 kg butadiene blend B-35. The jacket was heated to 57 °C. When the batch reached 57 °C, 5.0 mL of 1.68 M butyllithium diluted with about 20 mL of hexane were added. The polymerization exothermed after 15 minutes of reaction. After 2 hours, 5.0 mL more butyllithium and
10 subsequently 1.36 kg styrene blend were added to the reactor, still maintaining the jacket temperature at 57 °C. An exothermic peak was observed after 20 minutes. After 2 hr, 2.72 kg hexane was added, in order to favor the formation of micelles. After 20 min, 100 mL of divinylbenzene was added to the reaction mixture, in order to effect the cross-linking. After 16 hours of reaction, the reaction mixture was cooled down and
15 dropped in an isopropanol/acetone solution (about 500 mL/2L) containing BHT. The solid was then filtered through cheesecloth and drum-dried.

GPC analysis of the products, based on a polystyrene/THF standard, indicates the particles had the mean average molecular weight (M_n) of 1,337,100. The polydispersity index was 1.16, demonstrating that the particles had a relatively broader
20 distribution than in example 1.

Example 3.

The reactor was charged with 0.50 kg hexane and 1.04 kg butadiene blend B-35. The jacket of the reactor was heated to 57 °C. When the batch reached 57 °C, 5.0 mL of 1.68 M butyllithium diluted with about 20 mL of hexane were added. The

5 polymerization exothermed after 15 minutes of reaction. After 2 hours, 8.3 mL butyllithium and 1.8 kg styrene blend were added to the reactor, still maintaining the jacket temperature at 57 °C. An exothermic peak was observed after 20 minutes. After 2 hr, 2.72 kg hexane was added. After 20 min, 125 mL of divinylbenzene was added to the reaction mixture, in order to effect the cross-linking. After 16 hours of reaction, the

10 reaction mixture was cooled down and dropped in an isopropanol/acetone solution (about 500 mL/2L) containing BHT. The solid was then filtered through cheesecloth and drum-dried.

GPC analysis of the products, based on a polystyrene/THF standard, indicates the particles had the mean average molecular weight (M_n) of 1,437,376. The

15 polydispersity index was 1.78, demonstrating that the particles had a broader distribution than that of example 1 or example 2.

Example 4.

The reactor was charged with 0.50 kg hexane and 1.04 kg butadiene blend B-35.

20 The jacket of the reactor was heated to 57 °C. When the batch reached 57 °C, 5.0 mL of 1.68 M butyllithium were added. The polymerization exothermed at 57 °C after 15 minutes of reaction. After 2 hours, 15 mL butyllithium and 2.72 kg styrene blend were added to the reactor, while maintaining the jacket temperature at 57 °C. After 2 hr, 2.72

kg hexane was added. After 20 min, 150 mL of divinylbenzene was added to the reaction mixture, to effect cross-linking. After 16 hours of reaction, the reaction mixture was cooled down and dropped in an isopropanol/acetone solution (about 500 mL/2L) containing BHT. The solid was then filtered through cheesecloth and drum-dried.

5 Gel permeation Chromatography (GPC) analysis of the products, based on a polystyrene/THF standard, indicated the particles had two average molecular weight (M_n). One was around 1,254,950 and another was around 14,544,400. The polydispersity index was 1.92. The GPC results are shown in Figure 1. It should be noted that in the GPC analysis, however, the sample solution had an anomalous
10 difficulty passing through the GPC micro filter. This phenomenon indicated that some of the large particles had been cut-off by the GPC filter. The polydispersity index of 1.92, as measured by the GPC, might only, therefore, reflect part of the distribution. In order to more fully analyze the distribution, a transmission electron microscopy (TEM) analysis of the product was conducted (see FIG. 2). The TEM analysis was taken on a
15 toluene solution of the product at 10^{-5} wt% concentration. A drop of the diluted solution was then coated on a graphed copper micro-grid. After the solvent was vaporized, the screen was examined by TEM. The results showed that the product synthesized is a particle-like material and the average particle size was about 55 nm (Figure 1). The largest particle in this picture is about 120 nm; the smallest particle is about 10 nm. The
20 results demonstrated that the particles had a relatively broader distribution than that of example 1, 2 and 3. Interestingly, the particles/toluene solution (at ~ 20 wt.%) fluoresced a green color.

Example 5.

The process for producing nano-particles having a particular variety of particle size is preferably achieved by adjusting the ratio of conjugated diene to alkenylbenzene in the reactor. However, it should be noted that the ratio has a minimum boundary. The system can produce macroscopic gels, if the ratio is too small. An example is shown here for illustration.

The reactor was charged with 0.50 kg hexane and 1.04 kg butadiene blend B-35. The jacket was heated to 57 °C. When the batch reached 57 °C, 5.0 mL of 1.68 M butyllithium were added. The polymerization exothermed at 57 °C after 15 minutes of reaction. After 2 hours, 25 mL more butyllithium and 4.08 kg styrene blend were added to the reactor. After 2 hr, 2.72 kg hexane was added. After 20 min, 225 mL of divinylbenzene was added to the reaction mixture, to effect cross-linking. After 16 hours of reaction, the reaction mixture was cooled down and dropped in an isopropanol/acetone solution (about 500 mL/2L) containing BHT. The solid was then filtered through cheesecloth and drum-dried. The product contained 57.5 % of gelled material.

The invention has been described with reference to the exemplary embodiments. Modifications and alterations will occur to others upon reading and understanding the specification. The invention is intended to include such modifications and alterations insofar as they come within the scope of the disclosure and claims.